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Structure and Properties of Polymer Interphases

F. James Boerio
Department of Materials Science and Engineering
University of Cincinnati
Cincinnati, Ohio 45221

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The molecular structure of interphases between polymer systems and metal substrates was determined by using x-ray photoelectron spectroscopy (XPS), reflection-absorption infrared spectroscopy (RAIR), and attenuated total-reflection infrared spectroscopy (ATR) to characterize the failure surfaces of double cantilever beam adhesive joints prepared by curing beams of epoxies against metal beams. The structure of the interphases depended strongly on the curing agent, metal substrate, and use of a silane primer on the substrate. When joints were prepared by curing an epoxy with a tertiary amine curing agent at 75°C against a steel substrate primed with a dilute aqueous solution of γ -aminopropyltriethoxysilane (γ -APS), there was little reaction between the primer and adhesive and failure occurred near the primer/adhesive interface. The interphase consisted of low molecular weight siloxane oligomers in which the amino groups formed bicarbonates with water and carbon dioxide absorbed from the atmosphere. When similar joints were cured at 150°C, the bicarbonates dissociated, enabling the adhesive and primer to react, and shifting the locus

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of failure near the primer/adherend interface or into the epoxy. The interphase consisted of a crosslinked siloxane network in which amino groups of the primer were oxidized to imine groups.

More complex interphases were obtained when an epoxy was cured against primed substrates using an anhydride curing agent and a tertiary amine accelerator. The anhydride reacted with the amino groups of the primer to form amide and imide groups. Very close to the interface, carboxylate ions formed by reaction of the anhydride with the substrate. Segregation of the accelerator to the substrate surface was observed when the epoxy/anhydride adhesive was cured against copper but not when the same adhesive was cured against 2024 aluminum.

The use of surface-enhanced Raman scattering (SERS) for non-destructive characterization of interphases between polymers and metals was demonstrated. When a thick film of acrylic adhesive was cured against a silver substrate and examined using SERS, a strong Raman spectrum attributed to a metal salt of saccharin, a component of the adhesive cure system, was observed but there was no evidence of Raman scattering by the bulk adhesive. It was concluded that saccharin segregated to the metal surface, forming a salt, and that SERS could be used to characterize polymer/metal interphases without interference from normal Raman scattering by the bulk of the polymer.

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I. Introduction

A great deal of progress has been made in recent years in understanding the importance of the surface properties of the substrate in obtaining strong, durable adhesive bonds to metals. Adhesive bonds to aluminum provide an interesting case in point. Hydration of the oxide to pseudoboehmite is responsible for the failure of most adhesive bonds to aluminum during exposure to warm, moist environments (1). Anodizing aluminum in phosphoric acid provides a porous oxide that is very resistant to hydration in warm water (2). The resistance of the anodic oxide to hydration is due to the formation of a thin film of AlPO_4 on the outer surface and is essential for durability (3). The porosity of the oxide is important in determining the strength of the joint since it facilitates mechanical interlocking between the adhesive and the substrate. Somewhat similar results have been obtained for titanium anodized in chromic acid (4).

One aspect of the surface properties of the substrate that is not very well understood concerns the structure and properties of polymer interphases. Interphases represent the transition regions between polymer/substrate interfaces and the bulk of the polymer. As a first approximation, it is usually assumed that the properties of the interphase are the same as those of the bulk polymer. However, chemical and physical processes are influenced by interfaces and there may be a gradation of properties as the interface is approached but the extent of those structural gradations and their depth away from the interface and into the polymer are not well known.

Polymer interphases were discussed some time ago by Kumins and Kwei. Kumins (5) suggested that the mobility of a polymer in contact with a solid was different from that of the bulk polymer due to the adsorption of polymer segments onto the surface of the solid. Kwei (6) subsequently suggested that the effects of adsorption onto a filler particle could extend as far as 1500 Å into a polymer.

There has been little experimental evidence provided for the existence of polymer "interphases." However, Racich and Koutsky used transmission electron microscopy to show that the morphology of epoxy resins cured with polyamine curing agents was different in the bulk and near an interface (7). The morphology of the resin generally consisted of small nodules about 100 to 400 Å in diameter. Immediately adjacent to the adherend, there was a layer of closely packed smaller nodules while somewhat farther away (about 1000 Å) there was a layer in which the nodules were considerably larger. The high density of small nodules near the adherend surface was attributed to segregation of the curing agent. Similarly, the layer of large nodules somewhat farther away from the surface was attributed to depletion of the curing agent in that region.

Organofunctional silanes are widely used as primers for improving the durability of adhesive bonds between polymers and hydrophilic substrates such as glasses and metals. It is frequently considered that silanes function by forming chemical "bridges" between the substrate and the adhesive. However, it may be anticipated that in many cases a complex interphase will

be formed between the silane and the polymer, making this simple model of the way in which silanes function inadequate.

Numerous investigations of the characteristics of silane primer films have been reported which may be relevant to interphases. Chiang , used transmission infrared spectroscopy to study reactions between the components of an anhydride-cured epoxy and γ -aminopropyltriethoxysilane (γ -APS) between salt plates. He found that the anhydride curing agent reacted with γ -APS to form an imide, thereby eliminating the possibility of the silane forming a bridge between the substrate and the adhesive.

Boerio and Ondrus (9) showed that γ -APS formed amine bicarbonates by reaction with carbon dioxide and water in the atmosphere. Culler (10) showed that temperatures above 95°C were required to dissociate the amine bicarbonates that were formed during the application process. However, temperatures exceeding 120°C resulted in oxidation of the amino groups to imine groups.

Culler (10) investigated the reaction of an aminosiloxane primer with an epoxy resin between salt plates. Primer films were preheated for several minutes on salt plates at 120°C and then the epoxy resin was added. The reaction was followed with transmission infrared spectroscopy for two hours. Imine groups formed during preheating of the silane films and inhibited the reaction between the primer and the epoxy.

Few investigations of actual interphases involving silane coupling agents have been reported. However, Garton (11,12) used attenuated total reflection infrared spectroscopy (ATR) to characterize the molecular structure of an anhydride/epoxy

adhesive cured against a germanium crystal primed with an aminosiloxane coupling agent. He found that the amino groups of the siloxane reacted with the anhydride to produce amides but found no evidence of imide formation as observed by Chiang (8).

One of the primary objectives of this research is to determine the structure and properties of interphases in polymer/metal adhesive joints, especially when the metal substrates are pretreated with silane primers. The first step in this research was to determine the effect of metal substrates on the molecular structure of the primers. It was shown that copper and copper bearing alloys catalyzed the oxidation of the amino group of the primer (13). Aminosilane primer films applied to steel and titanium substrates oxidized to form imine groups when exposed to a temperature of 150°C for one hour in air atmospheres but did not oxidize when exposed to temperatures of 110°C. Imine formation occurred in the primer films on copper-containing substrates as a result of heating in air for one hour at the lower temperature. Commercially pure aluminum substrates inhibited the oxidation reaction. When γ -APS films were applied to 1100 aluminum and heated at 150°C for one hour, very little imine formation was observed.

It was also shown that epoxy films reacted with steel substrates primed with an aminosiloxane primer when cured at 150°C, but the epoxy film did not react with the siloxane primer that was applied to a copper-containing aluminum substrate (13). Steel and 2024 aluminum substrates primed with an aminosiloxane coupling agent were immersed in epoxy resin for one hour at

150°C. After cure, the substrates were rinsed with a solvent and examined using infrared spectroscopy. Retained epoxy was observed on the steel substrates but only the oxidized primer remained on the 2024 aluminum substrate. No retained epoxy was observed on either primed metal substrate when the cure temperature was lowered to 75°C for one hour. The infrared spectra of the substrates showed low molecular weight siloxane films containing amine bicarbonates.

We have also shown that the pH of the solution from which the primer was applied can affect the polymerization and reactivity of the film (9). Aminosiloxane primers deposited from basic solutions at pH 10.4 contained amine bicarbonates and formed low molecular weight siloxane oligomers. Primer films deposited from solutions acidified to pH 8.0 by addition of hydrochloric acid, contained amine hydrochlorides and formed higher molecular weight siloxane networks.

Aminosiloxane films applied to steel substrates from basic solutions (pH 10.4) reacted with epoxy resins when heated at 110°C. However, films applied from acidified solutions (pH 8.0) did not chemically react with the epoxy resin at the same temperature. After the samples were rinsed with solvent, the infrared spectrum of the film applied from the basic solution showed evidence of retained epoxy, but the spectrum of the film applied from the acidified solution showed only the cured siloxane network and amine hydrochlorides.

In this report, we describe the structure of interphases in actual adhesive joints prepared by curing epoxy resins against

metal substrates with and without primers applied to the substrates. Double cantilever beam (DCB) specimens were prepared by curing beams of epoxy resins against polished metal beams. After cooling from the post-cure, the residual stresses in these specimens were usually sufficient to enable starter cracks to be propagated along the interface, providing easy access to the adhesive and substrate failure surfaces for analysis by x-ray photoelectron spectroscopy (XPS) and by reflection-absorption and internal reflection infrared spectroscopy (RAIR and ATR, respectively). The results show that complex interphases are formed whose structure depends strongly on the curing agent, the metal substrate, and whether or not a silane primer is applied to the substrate.

The work on interphases using double cantilever beams requires that the epoxy beams be separated from the substrates for analysis. However, it is very desirable to develop non-destructive techniques for determining the molecular structure of polymer interphases. In this report we also describe preliminary results obtained using surface-enhanced Raman scattering as a non-destructive technique for characterizing polymer/metal interphases.

II. Experimental

Substrates for double cantilever beams (DCB) were machined from 2024-T3 aluminum and 1018 steel barstock to a final size of 0.25 x 0.50 x 7.50 inches, degreased with acetone, and then metallographically polished to obtain hydrophilic, specularly reflecting surfaces.

Initial polishing of the substrates was with a series of dry silicon carbide abrasive papers ranging from 240 to 600 grit. After the surfaces were ground, they were wet polished on microcloths (Beuhler, Inc.) with a 14 μm alumina slurry and either a 0.3 μm alumina slurry for the steel samples or 3.0 μm magnesium oxide slurry for aluminum samples. Finally, the substrates were rinsed in distilled deionized water and blown dry with a stream of nitrogen gas.

Half of the adherends were pretreated by being immersed in 1% aqueous solutions of γ -aminopropyltriethoxysilane (γ -APS) at pH 10.4 for one minute, withdrawn, and blown dry with a stream of nitrogen gas. The resulting primer films, which were about 100 \AA in thickness as measured by ellipsometry, were allowed to polymerize in the lab atmosphere at room temperature for thirty minutes before the adhesive was cast.

Two adhesive systems were considered. The first consisted of an epoxy resin (Epon 828, Shell Chemical Co.) cured with a tertiary amine (DMP-30, Miller-Stephenson) in a 100:6 ratio by weight. The second adhesive system consisted of the epoxy resin cured with nadic methyl anhydride (NMA, Fisher) and a tertiary amine accelerator, benzylidimethylamine (BDMA, Fisher), in a 100:100:2 ratio by weight. In both cases the epoxy resin was preheated to 60°C prior to addition of the curing agent and, if appropriate, accelerator.

DCB samples were produced by clamping an aluminum mold lined with sheets of fluorocarbon plastic around the polished adherend and casting the warm adhesive into the mold. The entire assembly

was then placed in an oven and cured at preselected temperatures and times. A chromel-alumel thermocouple was placed near the adherend/adhesive interface to monitor exotherms. After curing, the samples were removed from the mold and allowed to cool to room temperature overnight. The final dimensions of the DCB specimens are shown in Figure 1.

Due to differences in thermal expansion coefficients of the epoxy and the substrate, residual stresses at the interface were sufficient for cracks to be propagated very close to the interface. Sections two inches long were cut from the adhesive and adherend failure surfaces and analyzed using x-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared spectroscopy (ATR), and reflection-absorption infrared spectroscopy (RAIR).

Simulated polymer/metal interphases were created by reacting the epoxy/NMA adhesive without the BDMA accelerator with siloxane treated metal substrates. The primed metal mirrors were immersed in dishes filled with the unactivated adhesive then placed in a pre-heated oven at various temperatures and times. Following cure, the mirrors were removed from the resin mixture, allowed to cool, rinsed repeatedly with methylethylketone (MEK) to remove unreacted resin, and examined using RAIR.

Substrates were prepared for surface-enhanced Raman scattering by evaporating silver island films onto glass slides at the rate of about 1 Å per second to a final thickness of about 45 Å. Thin films of organic compounds such as saccharin were usually spin-coated onto the substrates from dilute solutions.

In a few cases an acrylic adhesive (monomer plus cure system) was simply swabbed onto the silver substrates.

Infrared spectra were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared spectrophotometer and external reflection accessories provided by Harrick Scientific. RAIR spectra were obtained using one reflection at an angle of 78°. 50 scans at 4.0 cm^{-1} resolution were averaged to obtain the spectra. Unless otherwise stated, the spectra reported are actually difference spectra obtained by subtracting spectra of clean polished substrates from spectra of sample surfaces. ATR spectra of the adhesive failure surfaces were obtained by pressing the surfaces against germanium ATR crystals. The angle of incidence was 45°.

XPS spectra of the failure surfaces were obtained using a Perkin-Elmer Model 5300 ESCA System. K_{α} radiation from a magnesium anode at a power of 300 watts was used to excite the spectra. Pass energy was 44.74 eV for survey spectra and 17.89 eV for multiplex spectra.

SERS and normal Raman spectra were obtained using a spectrometer equipped with a Spectra-Physics 165 argon-ion laser, Spex 1401 monochromator, and Harshaw photon-counting detection system. In most cases the slit width was 400 μm , the time constant was 10 sec, and the scan rate was 50 cm^{-1} per minute.

III. Results and Discussion

The RAIR spectrum from the adherend fracture surface of a DCB prepared using the epoxy/tertiary amine adhesive cast on a primed 1018 steel substrate and cured for two hours at 75°C, was

dominated by a strong band near 1120 cm^{-1} and weaker bands near 1040 , 1330 , 1470 , 1570 and 1640 cm^{-1} (see Figure 2). Bands near 1040 and 1120 cm^{-1} were assigned to SiOSi stretching modes (9). Those near 1330 , 1470 , 1570 , and 1640 cm^{-1} were related to amine bicarbonates formed by the reaction of the amino groups on the primer with water and carbon dioxide in the atmosphere (9). A weak band characteristic of epoxies was observed near 1510 cm^{-1} .

The bicarbonates did not dissociate during cure, thereby blocking the amino groups and preventing reaction between the primer and the adhesive. The interphase region consisted of a siloxane network in which the propylamine functional groups formed bicarbonates instead of chemical bridges with the adhesive.

When the curing reaction was carried out at 150°C for one hour, the RAIR spectrum obtained from the adherend failure surface was significantly different (see Figure 3A). Several bands associated with the epoxy were seen near 1605 , 1510 , 1260 , and 830 cm^{-1} . However, the intensity of these bands obscured the bands of the underlying interphase. In order to obtain spectra of the interphase, the spectrum of the epoxy was subtracted using the 1510 cm^{-1} band of the adhesive as a reference.

Normally, the RAIR spectrum from the adherend failure surface of an unprimed DCB sample would have been used to eliminate the adhesive and substrate phases. However, when DCB samples were prepared as described above using the epoxy/tertiary amine adhesive and unprimed substrates, complete interfacial failure always occurred and it was not possible to obtain the

RAIR spectrum of the adhesive on the metal substrate. Instead, an RAIR spectrum was obtained from a thin film of the epoxy/tertiary amine cast on a 1018 steel substrate from a dilute solution in MEK and cured for one hour (see Figure 3B). That spectrum was then subtracted from the spectrum in Figure 3A to obtain the spectrum of the interphase (see Figure 3C).

The spectrum in Figure 3C clearly shows the siloxane bands at 1040 and 1150 cm^{-1} . The latter band is shifted upward about 30 cm^{-1} relative to its position in the spectrum shown in Figure 2, indicating increased polymerization of the primer at the higher curing temperatures. The weaker band near 1660 cm^{-1} is due to the C=N stretching mode of imine groups formed by oxidation of the amino groups in the primer. The negative peak near 1740 cm^{-1} is due to a carbonyl stretching vibration resulting from oxidation of the thin adhesive film during curing against the steel substrate (see Figure 3B). The interphase in these specimens consisted of a highly crosslinked siloxane network in which the amino groups were oxidized to imines. There was no evidence of any unusual primer-adhesive interaction.

In DCB specimens prepared from primed substrates, failure occasionally occurred very near the metal/primer interface. RAIR spectra from the adherend failure surfaces showed no retained organic phase. In order to characterize the interphase in such specimens, the adhesive failure surfaces were examined. Figure 4A shows the ATR spectrum obtained from the adhesive failure surface of a DCB specimen prepared using the epoxy/tertiary amine adhesive cast on a primed 1018 steel substrate and cured at 150°C

for one hour. As expected, strong bands near 1605, 1510, 1260, and 830 cm^{-1} associated with the epoxy phase again obscured the spectrum of the interphase. Therefore, the ATR spectrum of the adhesive failure surface of a similar specimen prepared using an unprimed substrate (see Figure 4B) was obtained and subtracted from the spectrum in Figure 4A to obtain the spectrum of the interphase shown in Figure 4C. As usual, the 1510 cm^{-1} band was used as a reference in subtracting the spectra. The difference spectrum shows the siloxane bands near 1040 and 1150 cm^{-1} in addition to the imine band near 1660 cm^{-1} . This spectrum closely resembles the RAIR spectrum taken from the adherend side (see Figure 3C).

The interphases described above involved a two-component adhesive system. A more complex three-component system consisting of an epoxy resin, anhydride curing agent, and tertiary amine accelerator was also investigated. In this system, the epoxy can react with the curing agent, primer, or both. The curing agent can react with the epoxy, primer, or accelerator. Finally, the metal substrate may influence any of the reactions. Because of this complexity, reactions between various components of the adhesive system were also considered.

Figure 5A is an RAIR spectrum of a simulated adhesive interphase illustrating the reaction between the epoxy/anhydride adhesive and the siloxane primer on an aluminum mirror. The system was cured at 75°C for one hour and rinsed in MEK. The spectrum clearly shows two peaks at 1040 and 1150 cm^{-1} associated with the siloxane stretching frequencies of the primer. The

broad band near 1600 cm^{-1} could be an envelope of bands comprised of stretching vibrations from amide groups and carboxylate groups. Considering the absence of a sharp band near 1510 cm^{-1} , it was concluded that there was little epoxy retained.

When the cure temperature was raised to 150°C for one hour, the RAIR spectrum (Figure 5B) showed a sharp band near 1700 cm^{-1} in addition to the bands at 1040 , 1150 , and 1600 cm^{-1} . The 1700 cm^{-1} band was associated with the $\text{C}=\text{O}$ stretching vibration of a cyclic imide. The primary amine from the primer reacted with the anhydride group of the curing agent to form a cyclic imide. As a result, the functionality of the primer was reduced to zero and no chemical bridge was formed between the primer and the adhesive. Figure 5C shows that heating the system for 3 hours increased the intensity of the 1700 cm^{-1} band and reduced the intensity of the 1600 cm^{-1} band. This indicates that more cyclic imides were formed at the expense of the amide groups that were formed at lower temperatures.

The RAIR spectrum obtained from the adherend failure surface of a DCB sample prepared using a primed aluminum substrate and the epoxy/anhydride adhesive is shown in Figure 6A. The bands near 1510 and 1730 cm^{-1} are characteristic of the cured adhesive while the broad band near 1000 cm^{-1} may be associated with the oxidized aluminum substrate.

The RAIR spectrum of a thin film of the adhesive applied to an aluminum substrate from an MEK solution and cured is shown in Figure 6B. The band near 1730 cm^{-1} was assigned to the carbonyl

stretching mode of ester groups produced by the reaction between the anhydride and the epoxy.

The RAIR spectrum of the adherend failure surface from a DCB sample prepared using an unprimed aluminum substrate is shown in Figure 6C. The broad band near 1000 cm^{-1} is an envelope of bands due to oxidation products on the aluminum surface, including Al_2O_3 (960 cm^{-1}). The bands near 1600 and 1450 cm^{-1} are related to carboxylate vibrations due to salt formation between the curing agent and the aluminum.

Figure 6D is the difference spectrum obtained by removing the spectra of the adhesive (Figure 6B) and the substrate (Figure 6C) from the spectrum of the adherend failure surface (Figure 6A) and represents the interphase. Subtraction of the adhesive spectrum was based on the intensity of the band near 1730 cm^{-1} while subtraction of the substrate was based on the intensity of the broad band near 1000 cm^{-1} .

The spectrum of the interphase (Figure 6D) shows bands near 1650 and 1550 cm^{-1} characteristic of amide formation. The small band near 1700 cm^{-1} is due to the $\text{C}=\text{O}$ vibration of a cyclic imide. The sharp peak near 1780 cm^{-1} is the $\text{C}=\text{O}$ vibration from residual anhydride groups. The two bands near 1150 and 1040 cm^{-1} are the SiOSi vibrations from the siloxane network. The interphase region in this case contains amides, imides, residual unreacted curing agent and a crosslinked siloxane network.

Imide formation is contrary to the results found by Garton (12). However, the adhesive layers used by Garton were much thinner ($100\text{ }\mu\text{m}$) than those used here and were covered with a

Pyrex glass slide during curing. It is not clear if the amide group is part of a chemical bridge between the primer and adhesive or part of the amic acid precursor of the imide.

In order to determine if the curing agent forms a chemical bridge between the epoxy and the primer, the three components were reacted together in the bulk and analyzed with transmission infrared spectroscopy. Figure 7A is a spectrum of a 1:1 molar mixture of n-propylamine and NMA reacted at room temperature, dissolved in 2-propanol, and spread on a germanium window. The band near 1703 cm^{-1} is due to the carbonyl stretching vibration of the acid group of the amic acid product, and the two bands near 1650 and 1550 cm^{-1} are due to stretching vibrations of the amide group. Figure 7B is a spectrum of a 2:1 molar mixture of the amic acid and the epoxy resin reacted for 1 hour at 50°C and dissolved in MEK. The spectrum does not show a band near 1740 cm^{-1} associated with ester formation in the chemical bridge. After the mixture was heated to 150°C for 1 hour then dissolved in MEK, the spectrum of the product (see Figure 7C) showed a strong band near 1700 cm^{-1} and a weaker band near 1768 cm^{-1} associated with cyclic imide formation. Therefore, the imide formation is the favored reaction and no chemical bridging occurs between the aminofunctional primer and the epoxy adhesive through the anhydride curing agent in the bulk or at the interface.

As indicated above, carboxylate salts formed near the interface when the epoxy/anhydride adhesive was cured against 2024 aluminum. Compounds formed by reactions between components of adhesives and the substrate may have an important effect on

the properties of interphases. Accordingly, several experiments were conducted to characterize the reaction between NMA and metal oxides more completely.

In one case, thin films of NMA were applied to polished 2024 aluminum and OFHC copper mirrors. The mirrors were then heated at 150°C for two hours, cooled to room temperature, and rinsed with acetone. XPS and RAIR were then used to characterize the films. Bands were observed near 1610, 1460, and 960 cm^{-1} in RAIR spectra obtained from the films on the 2024 aluminum substrates (see Figure 8). The bands near 1610 and 1460 cm^{-1} were associated with stretching vibrations from carboxylate anions. The band near 960 cm^{-1} was attributed to lattice vibrations of the oxide.

In order to determine whether the salts formed by NMA on 2024 aluminum involved copper or aluminum cations, NMA was applied to copper mirrors and heated as described above. RAIR spectra obtained from the copper surfaces exhibited bands near 1550, 1420, and 645 cm^{-1} (see Figure 9). Those near 1550 and 1420 cm^{-1} were associated with the carboxylate anion and were shifted significantly from their positions in spectra obtained from the aluminum surface, indicating that the structure of the carboxylate species on copper and aluminum was different. It was tentatively concluded that the carboxylate species on 2024 aluminum involved aluminum cations. The band near 645 cm^{-1} was assigned to a lattice vibration of cuprous oxide (Cu_2O). Cupric oxide (CuO) is characterized by a strong band near 560 cm^{-1} but no significant absorption was observed near that frequency.

C(1s) XPS multiplex spectra of NMA films heated on copper substrates exhibited two bands separated by 3.5 eV (see Figure 10A). The band at lower binding energies was associated with adventitious carbon and with carbon bonded to carbon or hydrogen in the NMA films. The higher binding energy band was attributed to carbon triply bonded to oxygen in a metal-carboxylate complex.

Cu(2p) XPS multiplex spectra obtained from copper substrates having NMA films were complex (see Figure 10B) and indicated the presence of both Cu(I) and Cu(II) ions. The strongest bands in the spectra, near 932.0 and 952.4 eV, could be assigned to metallic copper or to Cu(I) ions. However, they were assigned to Cu(I) based on the modified Auger parameter which had a value of 1848.9 eV, very near that expected for Cu₂O. The bands near 933.8 and 954.3 eV and the satellites near 944.2 and 963.0 eV were assigned to Cu(II).

The results obtained from infrared spectroscopy thus indicated that the oxide on the copper substrates was mostly Cu₂O but the XPS results showed the presence of Cu(II) ions as well as Cu(I). Results from angle-resolved XPS showed that the Cu(II) ions were on the outermost surfaces of the samples, perhaps in a thin layer of CuO at the surface. However, the Cu(II) ions could also be associated with the carboxylate salts of the NMA curing agent.

C(1s) XPS multiplex spectra obtained from 2024 aluminum surfaces having NMA films were also characterized by two bands, but the separation was approximately 4.1 eV (see Figure 11). The difference in binding energy between the main C(1s) band and the

secondary band was thus about 0.6 eV higher for aluminum substrates than for copper substrates. As a result, it was concluded that the carboxylate species formed on 2024 aluminum involved the aluminum rather than copper ions. Moreover, the observed value of the modified Auger parameter for copper on the 2024 aluminum substrates having NMA films was 1852.3 eV, which suggests that copper formed the intermetallic precipitate CuAl₂ rather than a complex with NMA.

Once it was confirmed that NMA formed carboxylate salts on the surfaces of metals, the influence of the metal surface of the cured adhesive was investigated. Miniature DCB specimens were prepared by curing 1.0 inch thick beams of the epoxy with NMA and BDMA in a 100:100:2 ratio by weight against OFHC copper and 2024 aluminum substrates (0.5 x 1.0 x 0.0625 inches) for twenty four hours at 150°C. The beams were immersed in liquid nitrogen to induce fracture at the interface and the adhesive and adherend failure surfaces were examined using XPS. A "bulk" fracture surface from deep within the adhesive was also examined.

Carbon (78.3%), oxygen (21.2%), and a trace of nitrogen (0.5%) were observed on the bulk fracture surface. For the completely cured adhesive, the calculated composition was C(80.5%), O(19.5%) and N(0.1%).

The XPS survey spectrum taken from the adhesive failure surface of a DCB specimen prepared with a 2024 aluminum substrate had a composition similar to that of the bulk adhesive, with carbon (78.2%), oxygen (21.4%), nitrogen (0.4%), and a trace of

copper. Thus, no segregation of curing agent or accelerator to the interface was observed.

However, the adhesive failure surface of a DCB specimen prepared with a copper substrate was composed of C(76.1%), O(22.4%), and N(1.5%) and showed a threefold increase in nitrogen with respect to the bulk adhesive. It was concluded that the tertiary amine accelerator segregated to the interface when copper substrates were used.

All of the information regarding interphases that is described above was obtained using XPS, ATR, and RAIR to examine failure surfaces of DCB specimens. It is extremely desirable to develop non-destructive techniques for characterizing polymer interphases on a molecular level but there are few applicable analytical techniques. However, several preliminary experiments have been carried out which indicate that surface-enhanced Raman scattering (SERS) may be useful as a non-destructive probe for determining the structure of interphases in adhesive joints.

SERS is a process wherein the Raman scattering from molecules placed adjacent to the roughened surfaces of certain metals, such as copper, silver, and gold, is enhanced as much as six orders of magnitude. The enhancement for molecules farther away from the metal surface is much lower. The mechanisms responsible for the enhancement have been the subject of considerable debate but it is now generally agreed that most SERS can be attributed to an electromagnetic mechanism associated with large electric fields at the rough surfaces of metals and with charge-transfer complexes between metals and adsorbed molecules.

Since normal Raman scattering by polymers is usually quite weak but the enhancement for molecules next to metal surfaces is so great, it was considered that SERS might be used to characterize the interphase between a film of adhesive and a SERS-active substrate without interference from Raman scattering by the bulk of the adhesive as long as the adhesive film was less than about a thousand angstroms in thickness. Once the thickness of the adhesive film exceeds approximately a thousand angstroms, normal Raman scattering by the bulk of the film could become comparable in intensity to the SERS by molecules adsorbed onto the metal.

We have used SERS to examine the interphase between a model acrylic adhesive and a SERS-active silver substrate. The adhesive consisted of an acrylic monomer and a complex cure system containing saccharin and several other components.

The Raman spectrum of a film of adhesive about a thousand angstroms thick deposited onto a SERS-active silver film (see Figure 12A) was essentially identical to normal Raman spectra of the sodium salt of saccharin (see Figure 12B) and to Raman spectra obtained from thin films of saccharin deposited onto SERS-active silver substrates (see Figure 12C). It was concluded that saccharin from the adhesive was preferentially adsorbed at the silver surface to form a salt. Research is presently underway to determine the effect of salt formation at the interface on the rate of cure of the adhesive. No bands that could be attributed to normal Raman scattering by the bulk of the adhesive were observed in Figure 12A, indicating that SERS could

indeed be used for non-destructive characterization of polymer interphases in at least some applications.

IV. Conclusions

The molecular structure of the interphase region in adhesive joints made with aminosiloxane primed adherends varied as a function of curing agent and temperature. Joints made with tertiary amine-cured epoxy adhesives contained an interphase region which consisted of low molecular weight siloxane oligomers and amine bicarbonates when cured at 75°C. There was little reaction between the primer and adhesive, and failure occurred near the primer/adhesive interface.

In joints made with the same adhesive system cured at 150°C the interphase region consisted of a highly crosslinked siloxane network and imines. There was no evidence of secondary amine formation which is indicative of chemical interaction between the siloxane and the epoxy. However, the locus of failure was near the primer/adherend interface or in the epoxy, indicating good bonding between the primer and adhesive.

Adhesive joints prepared with the anhydride curing system had a more complex interphase than those using the tertiary amine system. With the anhydride system, the interphase consisted of a crosslinked siloxane network with amide and imide groups formed by reaction of the anhydride with the amino groups of the silane primer. Very close to the interface, carboxylate ions formed by reaction of the anhydride with the substrate were also found. Segregation of the accelerator to the substrate surface was

observed when the epoxy/anhydride adhesive was cured against copper but not when the same adhesive was cured against aluminum.

Surface-enhanced Raman scattering can be used for non-destructive characterization of interphases between polymers and metals such as copper, silver, and gold which are SERS-active. When an acrylic adhesive was cured against a silver substrate, results obtained from SERS showed that saccharin, which was a component of the adhesive cure system, segregated to the surface and formed a silver salt.

VI. References

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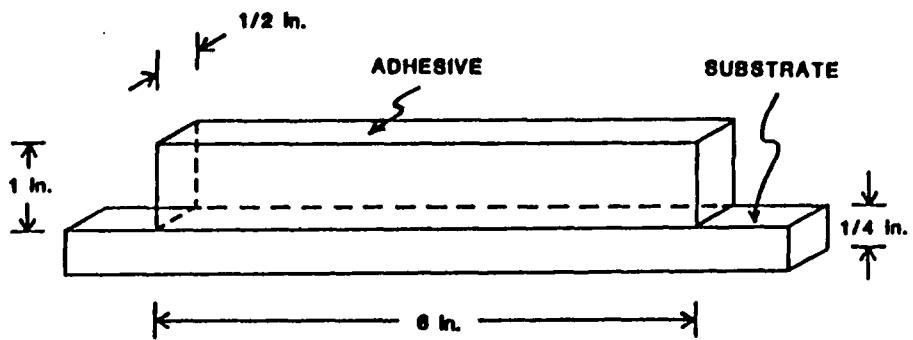


Figure 1. Double cantilever beam specimen.

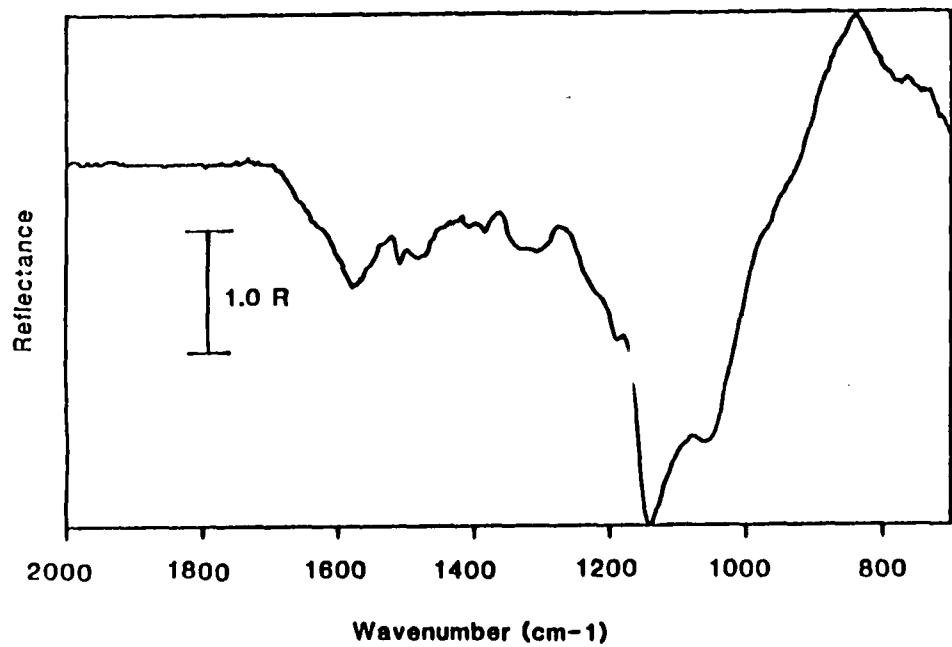


Figure 2. RAIR infrared spectrum of the substrate failure surface of a DCB specimen prepared from a steel substrate and an epoxy cured at 75°C for one hour with a tertiary amine. The substrate was primed with a dilute aqueous solution of γ -APS.

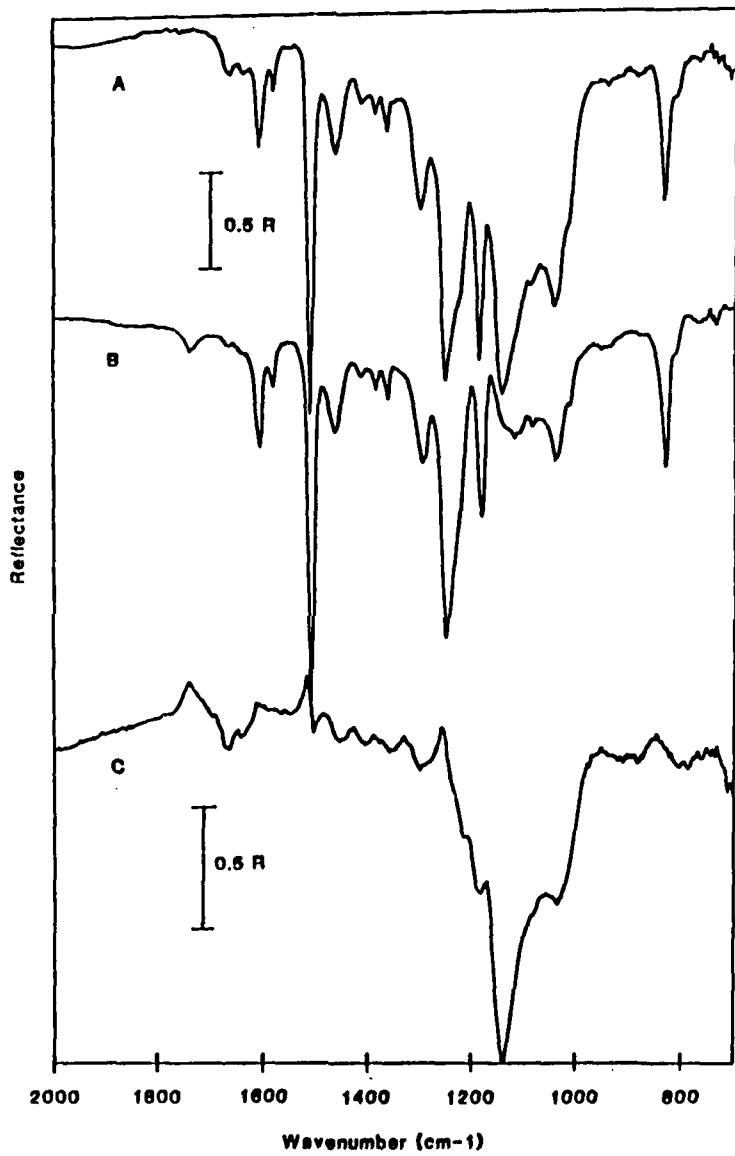


Figure 3. RAIR spectra of (A) - the failure surface of a DCB prepared from a steel substrate primed with γ -APS and an epoxy cured with a tertiary amine curing agent, (B) - a film of the same epoxy deposited on a polished steel substrate, and (C) - the difference of A and B. In A and B the epoxy was cured at 150°C for one hour.

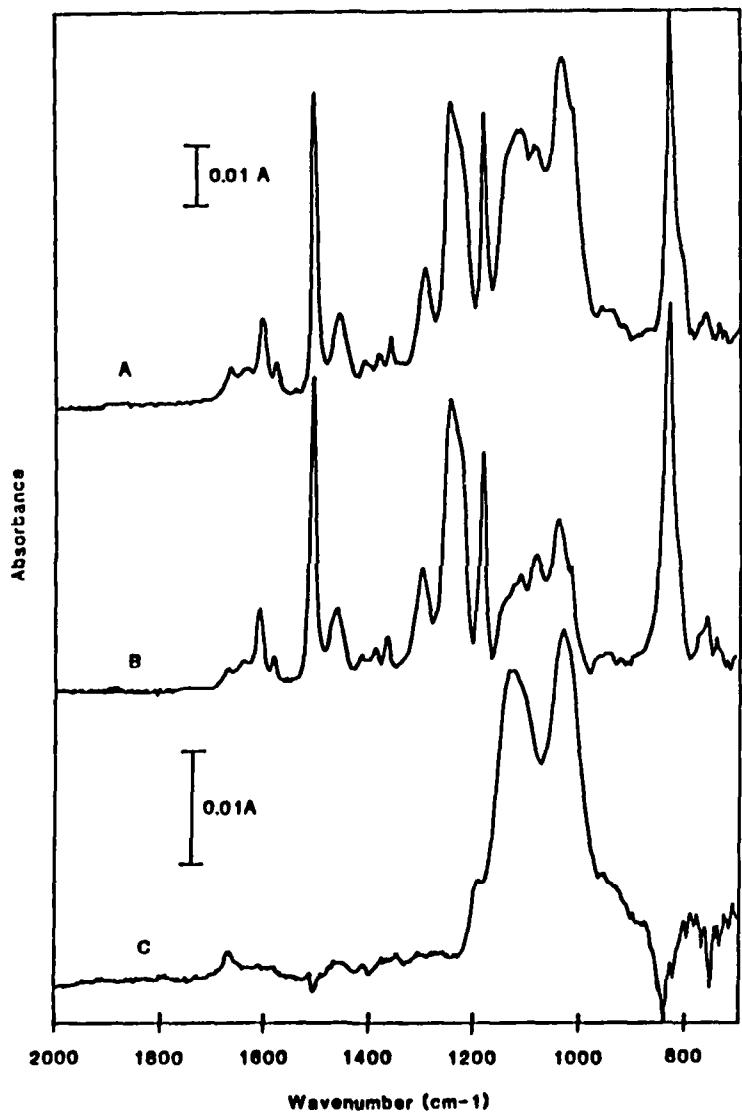


Figure 4. ATR infrared spectra of the adhesive failure surfaces of DCB specimens prepared from steel substrates and the epoxy cured with a tertiary amine at 150°C for one hour; (A) - substrate primed with a dilute aqueous solution of γ -APS, (B) - substrate unprimed, and (C) - the difference of A and B.

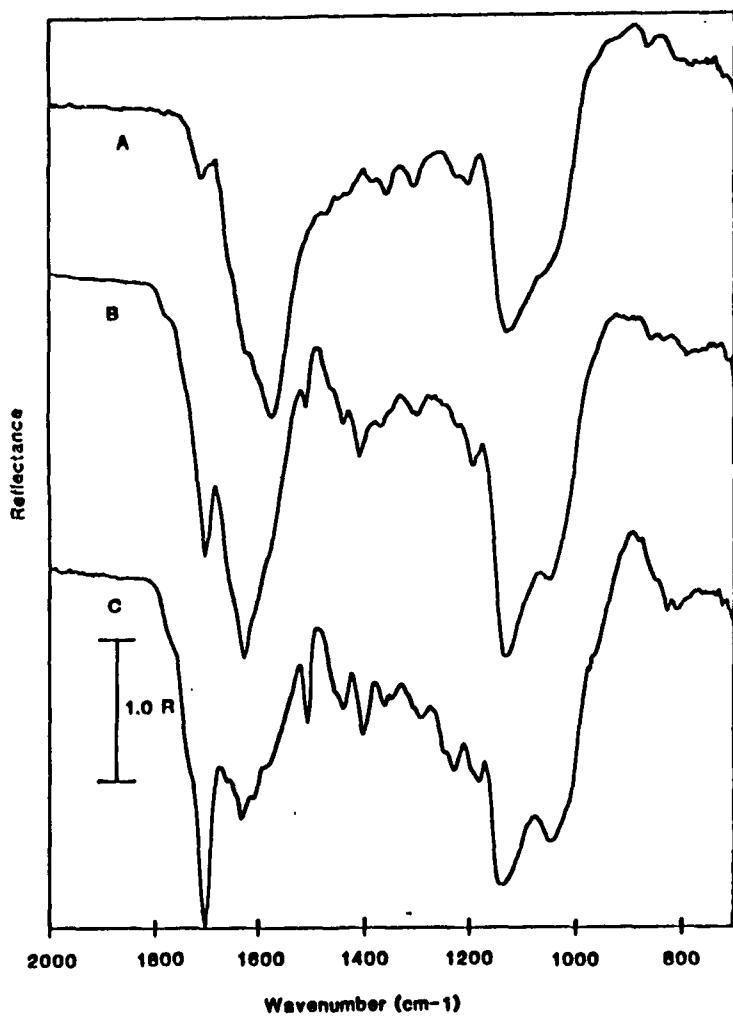


Figure 5. RAIR spectra obtained from 2024 aluminum mirrors that were primed with dilute aqueous solutions of γ -APS and then reacted with a mixture of epoxy resin and nadic methyl anhydride (NMA) at (A) - 75°C for one hour, (B) - 150°C for one hour, and (C) - 150°C for three hours and then rinsed with methylethylketone.

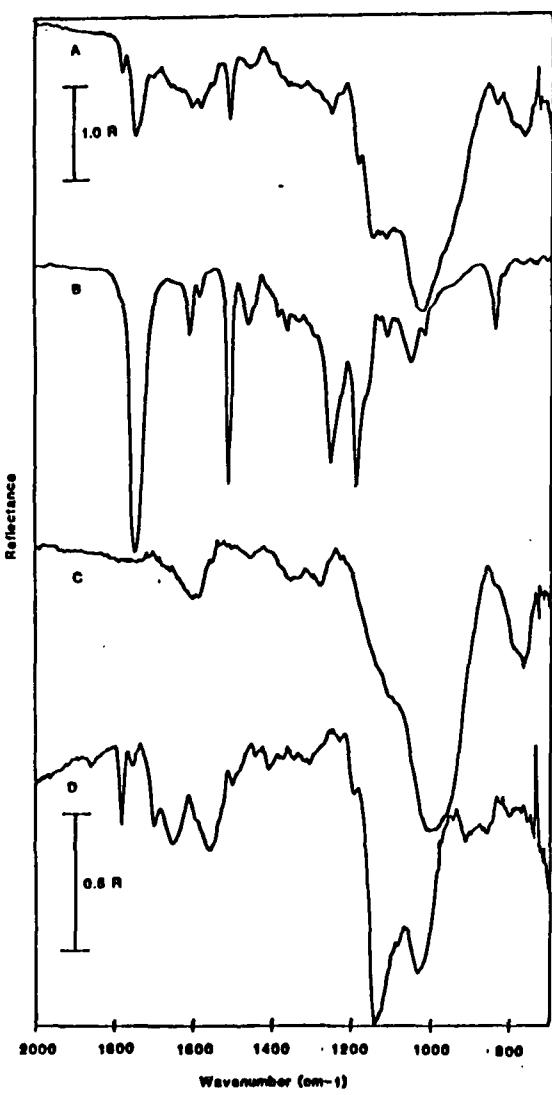


Figure 6. RAIR spectra obtained from (A) - the substrate failure surface of a DCB specimen prepared by curing a beam of the epoxy/anhydride at 150°C for two hours against a 2024 aluminum beam primed with γ -APS, (B) - a thin film of the epoxy/anhydride applied to a 2024 aluminum mirror and cured, (C) - the substrate failure surface of a DCB specimen that was cured against an unprimed 2024 aluminum beam, and (D) - the difference of A, B,

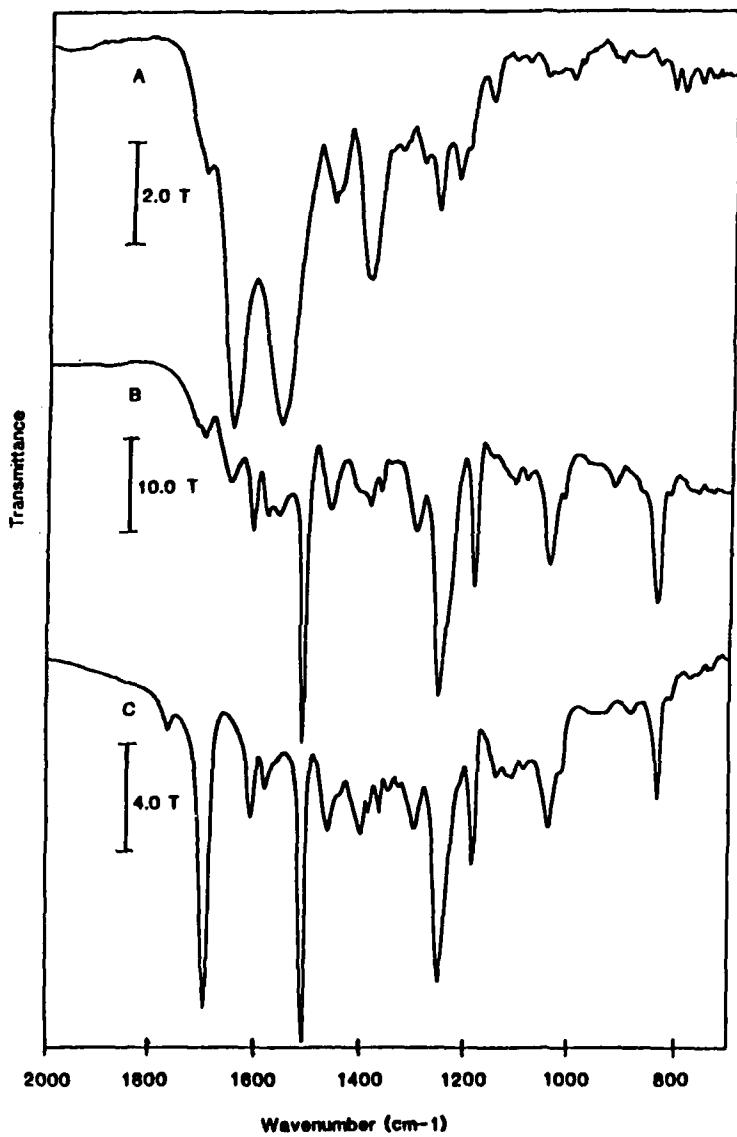


Figure 7. Transmission infrared spectra of (A) - the amic acid obtained by reacting a 1:1 molar mixture of NMA and n-propylamine, (B) - the products obtained by reacting a 2:1 molar mixture of the amic acid and the epoxy resin for one hour at 50°C, and (C) - the sample in B heated at 150°C for an additional hour.

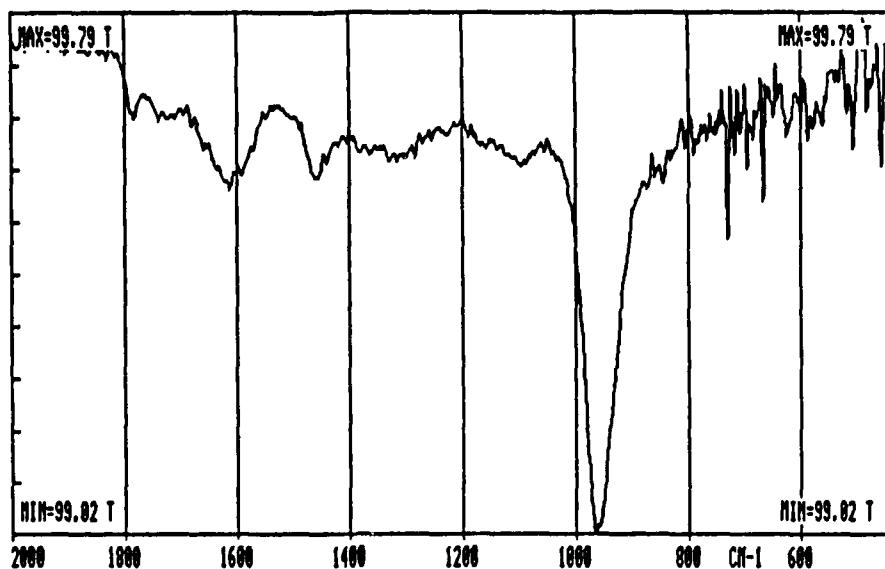


Figure 8. RAIR spectrum obtained from a thin film of NMA that was applied to a polished 2024 aluminum mirror, heated for two hours at 150°C, and then rinsed with acetone.

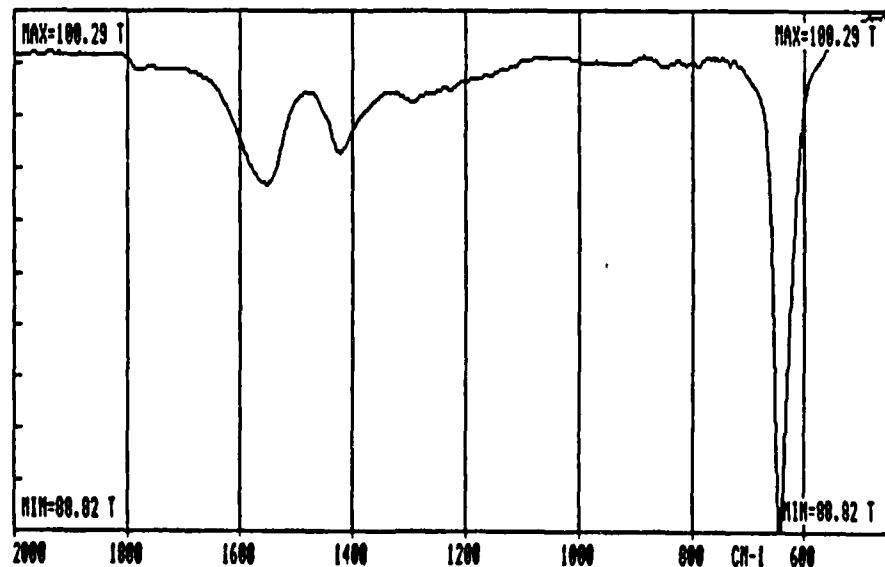
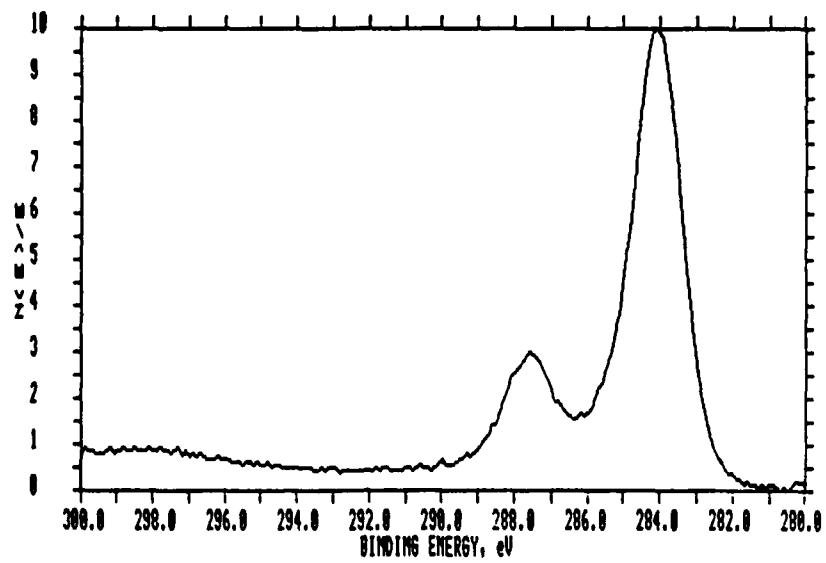
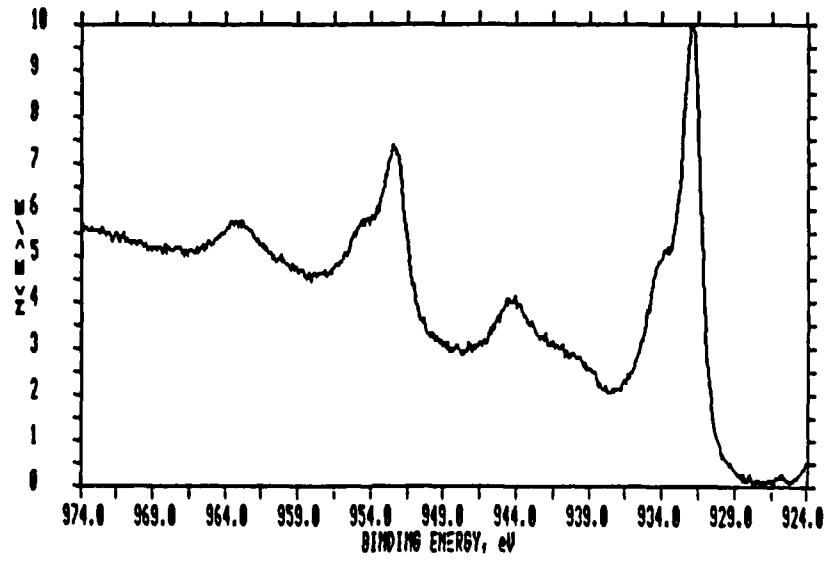


Figure 9. RAIR spectrum obtained from a thin film of NMA that was applied to a polished copper mirror, heated for two hours at 150°C, and then rinsed with acetone.



(A)



(B)

Figure 10. (A) - C(1s) and (B) - Cu(2p) XPS multiplex spectra obtained from an NMA film applied to copper, heated at 150°C for two hours, and rinsed with acetone.

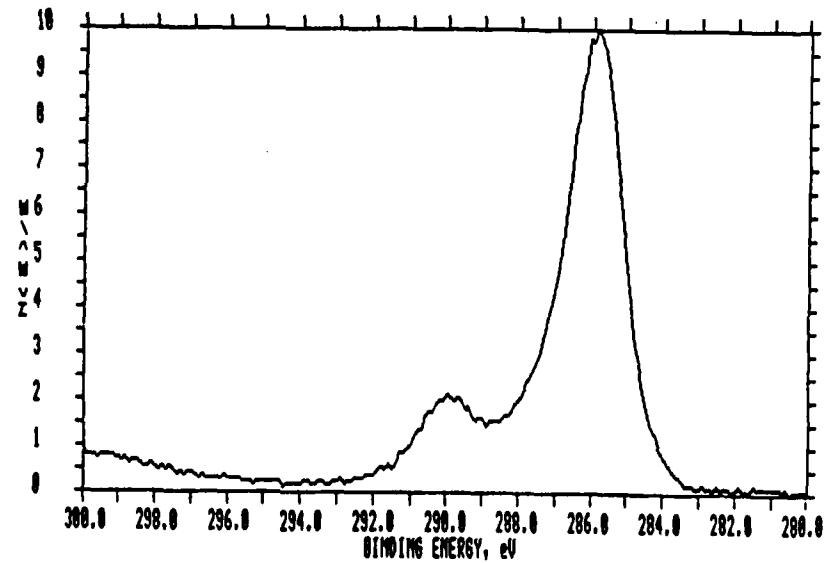


Figure 11. C(1s) XPS multiplex spectrum obtained from an NMA film coated on a 2024 aluminum mirror, heated at 150°C for two hours, and rinsed with acetone.

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Austin, TX 78746

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Naval Weapons Center
Attn: Mr. A. Amster
China Lake, CA 93555

Professor S. Wang
Dept. of Theoretical & Applied Mechanics
University of Illinois
Urbana, IL 61801

Dr. J. D. Venables
Martin Marietta Laboratories
1450 South Rolling Road
Baltimore, MD 21227

Dr. R. W. Seibold
Hughes Aircraft Co.
Bldg E4 MS F150
P.O. Box 902
El Segundo, CA 90245

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Prof. J. P. Wightman
Prof. J. N. Reddy
Prof. D. A. Dillard
Center for Adhesion Science
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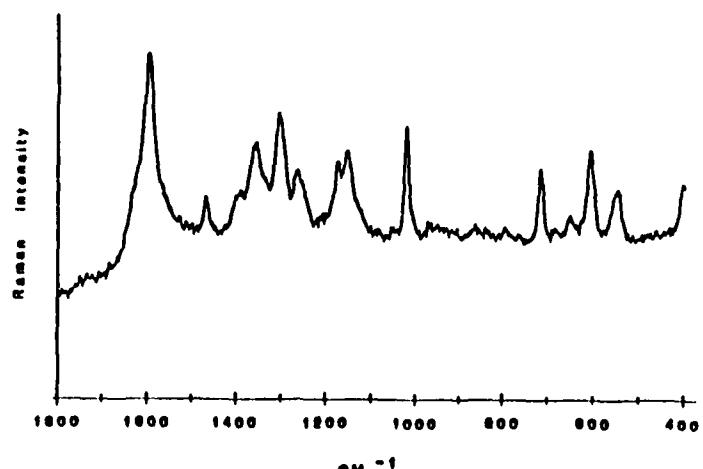
Prof. A. N. Gent
Institute of Polymer Science
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Akron, OH

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Dept. of Macromolecular Science
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Cleveland, OH 44106

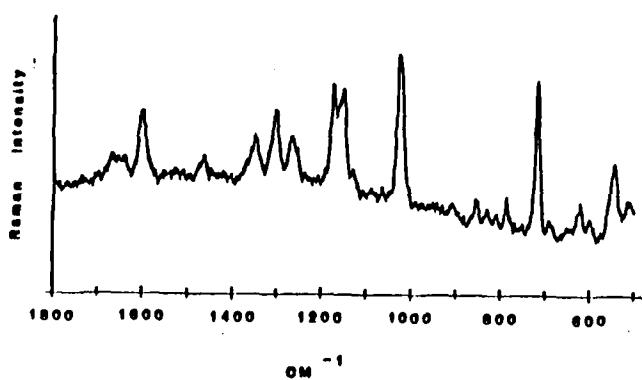
Professor F. J. Boerio
Dept. of Materials Science
University of Cincinnati
Cincinnati, OH 45221

Dr. J. Ahearn
Martin Marietta Laboratories
1450 South Rolling Road
Baltimore, MD 21227

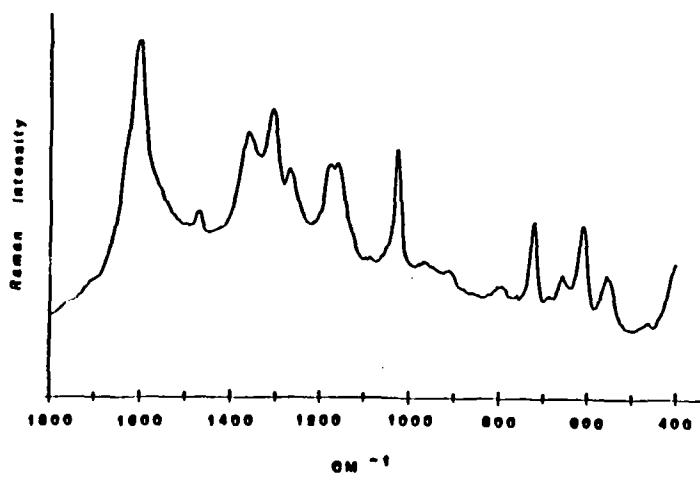
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(A)



(B)



(C)

Figure 12. (A) - Surface-enhanced Raman scattering from a thick film of acrylic adhesive deposited onto a silver substrate, (B) - normal Raman scattering from the sodium salt of saccharin, and (C) - SERS from a thin film of saccharin deposited on silver.